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Radon and Radium Isotopes, Groundwater Discharge and Harmful Algal Blooms in Little Lagoon, Alabama

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Abstract—Naturally-occurring radon (^{222}Rn) and radium isotopes (^{223,224,226,228}Ra) were used as tracers to study possible relationships between submarine groundwater discharge (SGD) and microalgal population dynamics in Little Lagoon, Alabama (USA). We evaluated SGD inputs based on a mass balance of "excess ^{226}Ra," the amount above that contributed from Gulf of Mexico (GOM) waters. The study area was divided into east, west and central areas and had estimated SGD rates of 1.56, 0.91 and 0.61 m^3 s^{-1}, respectively. Groundwater nutrient concentrations were extremely high with total N concentrations up to 945 μM and N/P molar ratios up to ~500. Since there are no significant surface water inputs to the lagoon, SGD must dominate the supply of new nutrients. The ratio of the phytoplankton pigments zeaxanthin to fucoxanthin (a proxy of the abundance of cyanobacteria relative to diatoms) measured in the water column was highly correlated (r = –0.84) with ^{224}Ra/^{223}Ra activity ratios, a proxy for water 'age'. Because the source of these short-lived isotopes is groundwater, this suggests that SGD is a significant driver of phytoplankton community composition in Little Lagoon.

Keywords: radium isotopes, radon, submarine groundwater discharge, phytoplankton, Little Lagoon

INTRODUCTION

It is now recognized that the transport of land-derived chemical species through submarine groundwater discharge (SGD) can rival that via river runoff (Burnett *et al.*, 2003; Swarzenski *et al.*, 2006). Nutrients delivered by SGD can affect the phytoplankton community composition in coastal areas (Lee and Kim, 2007). Excess nutrient inputs via SGD may cause coastal water and benthic macro-algal eutrophication (Valiela *et al.*, 1990; Hwang *et al.*, 2005) which has been correlated

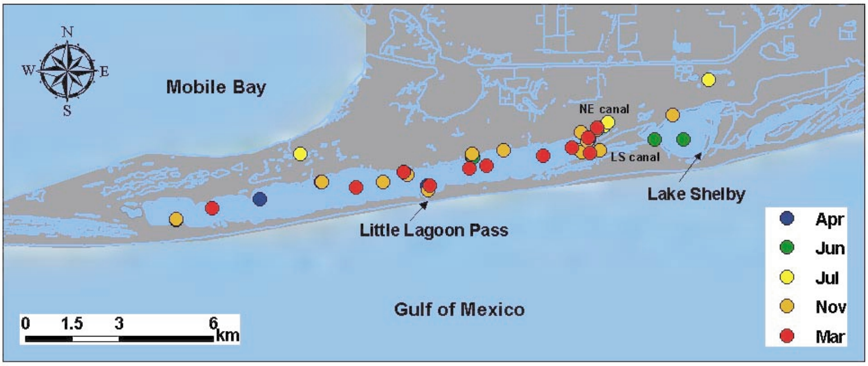

Fig. 1. Sampling stations for radium isotopes in Little Lagoon, Alabama from April 2010 to March 2011. Samples on land are monitoring wells.

with harmful algal blooms (HABs) (Anderson *et al.*, 2002).

Little Lagoon, in Baldwin County, Alabama (USA), is a hot-spot for toxic blooms of the HAB diatom *Pseudo-nitzschia* spp. both at Little Lagoon Pass (Liefer *et al.*, 2009) and in the littoral Gulf of Mexico west of the lagoon (MacIntyre *et al.*, 2011). The density of blooms is highly correlated with discharge from the surficial aquifer (Liefer *et al.*, 2009). We report here on the use of natural radioisotopes to discern the patterns and amounts of SGD in the lagoon.

SAMPLING AND METHODS

Study area

Little Lagoon is a shallow enclosed coastal lagoon with an average water depth of ~1.5 m and a surface area of ~9.3×10^6 m^2. The lagoon is connected to the Gulf of Mexico (GOM) by a pass 15 m wide and 1 m deep. Lake Shelby canal (hereafter LS canal) at the east end of lagoon connects the lagoon to Lake Shelby, a small brackish-water lake. Another canal is located in the northeast sector of the lagoon (hereafter NE canal). The lagoon lacks stream inputs but is likely to have significant groundwater inputs because of a local maximum in groundwater elevation (Dowling *et al.*, 2004; Murgulet and Tick, 2008). The unconfined aquifer here is typical of coastal plain deposits throughout much of the GOM consisting of coarse-grained quartz sands, with varying degrees of heavy minerals, shell fragments, and silt. The primary source of recharge for this aquifer comes from local precipitation (annual precipitation = 167 cm yr^{-1}) infiltrating the surface sands (Dowling *et al.*, 2004).

Measurement of radium isotopes (^{223,224,226,228}Ra) and ^{222}Rn

Surface water samples (*ca.* 60 L) were collected for radium isotope analysis

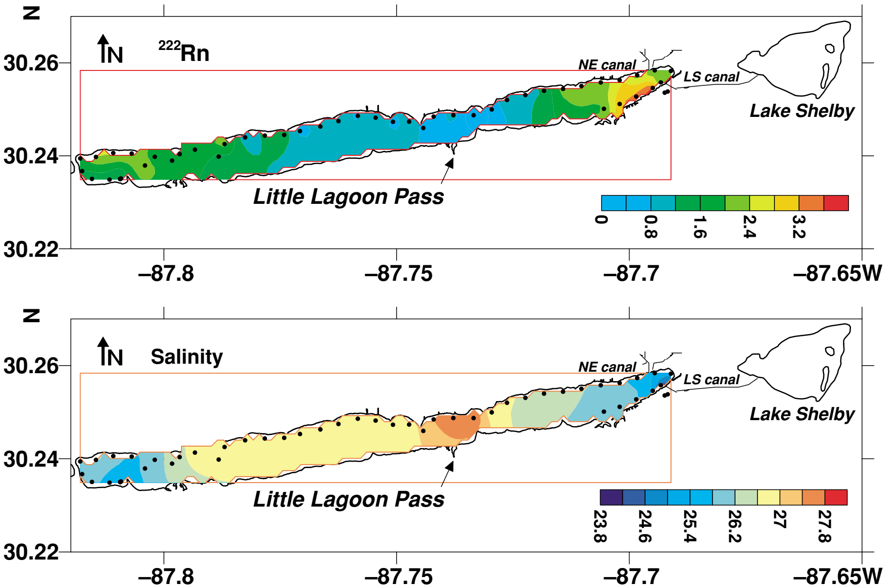

Fig. 2. Distribution of ^{222}Rn concentrations (dpm L^{-1}) and salinity (dimensionless) throughout Little Lagoon on May 27, 2010.

in Little Lagoon (LL), Lake Shelby (LS), canals (C), and monitoring wells (GW) around the lagoon in April, June, July, November 2010 and March 2011 (Fig. 1). Radium isotopes were extracted onto Mn-fibers by standard techniques (Moore, 1976), analyzed for short-lived ^{223}Ra and ^{224}Ra via a RaDeCC system (Moore and Arnold, 1996), and analyzed for long-lived ^{226}Ra and ^{228}Ra via gamma spectrometry (Dulaiova and Burnett, 2004). ^{224}Ra activities were corrected for that supported by its parent ^{228}Th, and ^{224}Ra activities reported here are all "excess."

^{222}Rn activities in lagoon waters were measured continuously with an automated pumping and sparging system connected to a suite of three RAD-7 detectors for real-time *in-situ* analysis (Burnett *et al.*, 2001; Dulaiova *et al.*, 2005). The system is integrated with a CTD Diver (Van Essen) and logging GPS with depth sounding capabilities. Samples collected on Whatmann GF/F filters were analyzed by high performance liquid chromatography (HPLC) for the abundance of plant pigments.

RESULTS AND DISCUSSION

Groundwater sources revealed by ^{222}Rn

Radon is a useful tracer for exploring sources of groundwater discharge, allowing identification of areas for more extensive studies to quantify the groundwater input rates (Santos *et al.*, 2008). The radon survey conducted on

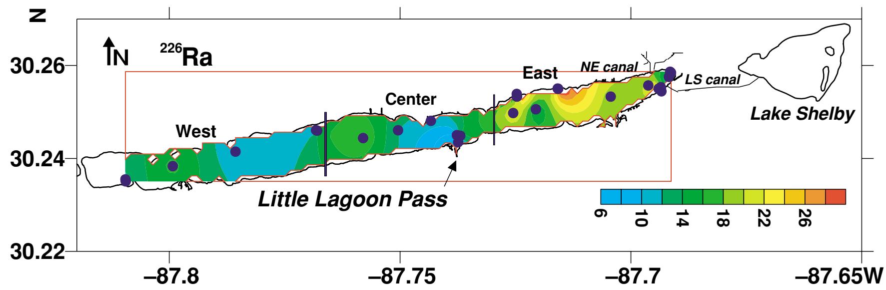

Fig. 3. Concentrations of ^{226}Ra (dpm 100L^{-1}) in Little Lagoon. Note the closed circles are sampling stations and the two vertical bars divide the study area into three segments.

May 27, 2010 concentrated on the north shore, eastern and western ends of the lagoon. The results showed that there were Rn and salinity gradients with both ends of the lagoon having higher Rn and lower salinities (Fig. 2). Low salinity water in the lagoon is derived from two fresh water inputs, SGD and Lake Shelby via the canal. Since groundwater is characterized by high Rn, these results demonstrate that there were likely SGD sources at both ends of the lagoon, especially in the east end. The high radon concentrations observed in these areas also suggest that groundwater-derived nutrients and other constituents may enter the lagoon via groundwater pathways. Nutrient data (Liefer *et al.*, 2011) showed that groundwater N was extremely high with total N (TN) concentrations up to 945 μM and N/P molar ratios up to ~500. Thus any SGD will likely be accompanied by significant nutrient inputs.

Spatial distribution of Ra isotopes

Since the spatial distribution of all four Ra isotopes show similar trends, we only present the results of ^{226}Ra here. In a manner similar to that observed for Rn, the highest ^{226}Ra activities were also at the eastern end of the lagoon, decreasing towards the center, and increasing slightly towards the west end of the lagoon based on all our measurements from April 2010 to March 2011 (Fig. 3).

Figure 4 shows the relationship between ^{226}Ra and salinity. It is evident that almost all LL samples are significantly enriched in ^{226}Ra over GOM waters. Linear regression of ^{226}Ra activities versus salinity for the LL samples suggested a groundwater end-member with ^{226}Ra concentration of 53 ± 14 dpm 100 L^{-1} ($p < 0.05$). This is within the lower range of ^{226}Ra activities measured in samples from groundwater wells, which ranged from 42 to 157 dpm 100 L^{-1}. Although there were large variations in the groundwater ^{226}Ra observed thus far, there were 2 groundwater well samples with ^{226}Ra concentrations close to the regression intercept. One of these wells is at the east end of the lagoon near the NE canal, whereas the other one is on the north shore, ~8.0 km away. The LS samples fell into a separate grouping, all higher in ^{226}Ra activities than GOM waters.

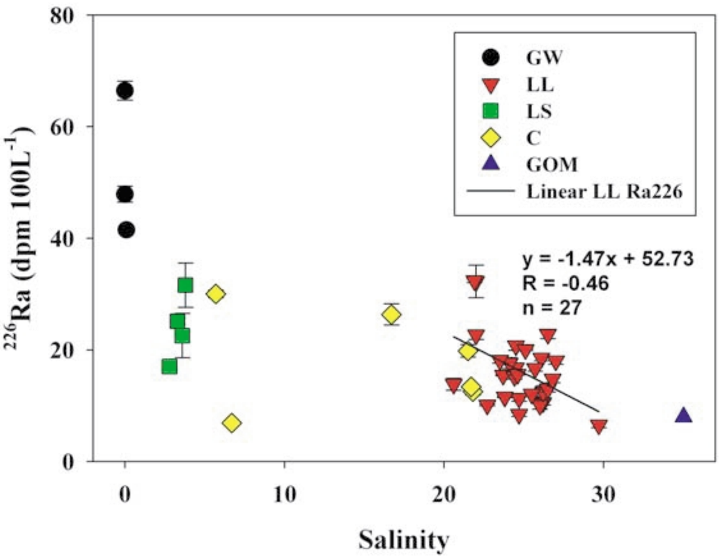

Fig. 4. ^{226}Ra versus salinity from water samples in Little Lagoon (LL), Lake Shelby (LS), canals (C), fresh groundwater (GW) and Gulf of Mexico (GOM). Groundwater samples with higher activities (>80) are not included (mean of the high samples = 126 ± 43 dpm 100 L^{-1}, n = 4).

Radium "ages"

Naturally-occurring radium isotopes can be used to determine the apparent ages of coastal water masses based on an activity ratio (AR) of a short-lived to a longer-lived Ra isotope (Moore, 2000). Radium that has recently entered a water body will have a higher AR that will then decrease as a function of radioactive decay and mixing. Since the mixing would be the same for both isotopes, decay time will be the dominate control and can be calculated via the following expression (for the case ^{224}Ra/^{223}Ra AR):

$$\left[\frac{^{224}\mathrm{Ra}}{^{223}\mathrm{Ra}}\right]_{\mathrm{obs}} = \left[\frac{^{224}\mathrm{Ra}}{^{223}\mathrm{Ra}}\right]_{\mathrm{i}} \cdot \frac{e^{-\lambda_{224}t}}{e^{-\lambda_{223}t}} \qquad (1)$$

where $[^{224}\mathrm{Ra}/^{223}\mathrm{Ra}]_{\mathrm{obs}}$ represents the measured activity ratio of the sample, $[^{224}\mathrm{Ra}/^{223}\mathrm{Ra}]_{\mathrm{i}}$ is the initial activity ratio of the radium that entered the system, λ_{224} and λ_{223} are the decay constants for ^{224}Ra and ^{223}Ra (λ_{224} = 0.189 day^{-1}, λ_{223} = 0.0606 day^{-1}), respectively, and t is the time since the water became enriched in Ra and is isolated from its source. This approach assumes: (1) the initial ^{224}Ra/^{223}Ra (or other AR) is constant; (2) there is only one Ra source; (3) no additions or losses of Ra occur except for mixing and radioactive decay after the water leaves the source region; and (4) the open Gulf contains negligible excess ^{224}Ra and ^{223}Ra.

Because the AR in the groundwater samples varied within a wide range, we do not have a good estimate of the initial AR at this time. Thus, we use the highest LL value measured for each suite of samples in different sampling periods to calculate relative Ra ages. Because we use the highest AR in LL rather than in the GW source, the calculated Ra ages are underestimated. However, these results will provide correct relative age differences between samples which are independent of the initial AR. Based on Eq. (1) and its assumptions, the lowest Ra ages (0.4–2.4 days) were observed in the east end of the lagoon, consistent with a Ra source in that area.

SGD estimates based on a ^{226}Ra mass balance model

Many researchers have applied a Ra mass-balance to estimate SGD (Moore, 1996; Kim *et al.*, 2005; Swarzenski *et al.*, 2007). Since groundwater discharge in the lagoon is the only likely dominant source of Ra, the activities of ^{226}Ra above the baseline supported by GOM waters should represent the contribution from SGD.

$$\mathrm{SGD}\left(\mathrm{m^3\ days^{-1}}\right) = \frac{\mathrm{Excess}\ ^{226}\mathrm{Ra}\left(\mathrm{dpm\ m^{-3}}\right)\cdot \mathrm{vol}\left(\mathrm{m^3}\right)}{\tau\left(\mathrm{days}\right)\cdot \mathrm{gw}^{226}\mathrm{Ra}\left(\mathrm{dpm\ m^{-3}}\right)} \tag{2}$$

where the excess ^{226}Ra is the amount above that contributed by GOM waters; vol is the volume of the water body; τ is the water residence time; gw^{226}Ra is the ^{226}Ra activity in the groundwater end-member. Assuming conservative behavior, excess ^{226}Ra is calculated as follows:

$$\mathrm{Excess}\ ^{226}\mathrm{Ra} = {}^{226}\mathrm{Ra_{obs}} - \left({}^{226}\mathrm{Ra_{GOM}} \times \frac{S_{\mathrm{obs}}}{S_{\mathrm{GOM}}}\right) \tag{3}$$

where $^{226}Ra_{obs}$ and S_{obs} are the measured ^{226}Ra activity and salinity in Little Lagoon samples, and $^{226}Ra_{GOM}$ and S_{GOM} are the known ^{226}Ra activity and salinity in GOM waters ($^{226}Ra_{GOM}$ = 8.0 dpm 100 L^{-1} and S_{GOM} = 35.0) (Moore and Scott, 1986). Since the ^{226}Ra concentrations in the groundwater samples measured thus far varied over a wide range, we used the y-intercept value based on our regression of ^{226}Ra versus salinity (gw^{226}Ra = 53 dpm 100 L^{-1}, Fig. 4). We estimated an overall residence time of ~10 days for lagoon waters based on a tidal flushing model (Monsen *et al.*, 2002). Residence times for different portions of the lagoon are currently under investigation.

We divided our study area into east, west and central areas based on the Rn and Ra distributions shown earlier. Using Eq. (3), the excess ^{226}Ra activities are 15.4, 5.81 and 6.95 dpm 100 L^{-1} in the east, west and center segments, respectively. The estimated volumes of these respective segments are 3.1×10^6, 3.2×10^6 and

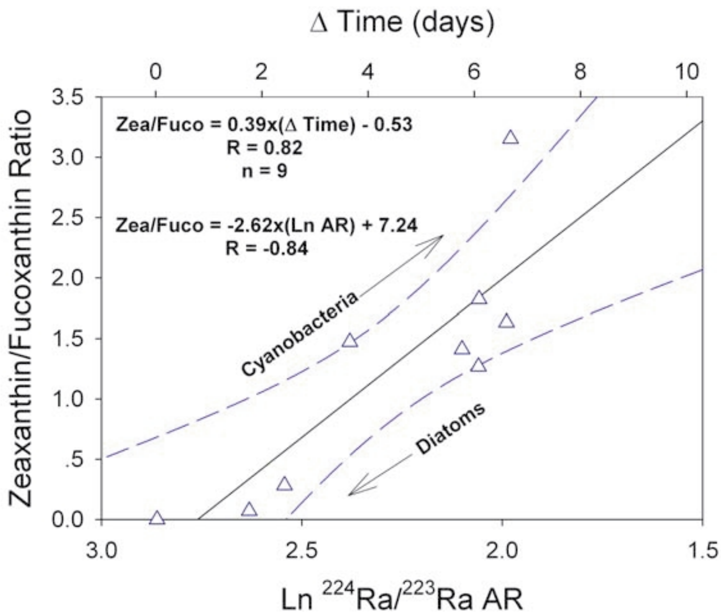

Fig. 5. The relationship between the pigment-specific ratio (zeaxanthin/fucoxanthin) vs. the Ln $^{224}Ra/^{223}Ra$ activity ratio and 'age' for the samples collected in April 2010. The radium ages were calculated based on an assigned "initial" ratio which was the highest value observed within the sample set.

4.0×10^6 m^3. Applying these parameters to Eq. (2) yielded SGD rates of 1.56 m^3 s^{-1} in the eastern end, 0.91 m^3 s^{-1} in the western segment and 0.61 m^3 s^{-1} in the central area. Based on these results, the turnover time for lagoon waters if they were only replaced by groundwater can be estimated by dividing the volume of the lagoon segments by the respective SGD rates. The resulting times of 23, 50 and 60 days in the east, west and central areas, respectively, are clearly much longer than the estimated tidal flushing time of ~10 days. So while SGD is an important nutrient pathway to Little Lagoon, the discharge rates are relatively unimportant in terms of flushing of the lagoon.

Relationship between SGD and microalgal community composition

The two dominant pigments were fucoxanthin and zeaxanthin, which are taxonomic markers for diatoms and cyanobacteria, respectively. The ratio of zeaxanthin to fucoxanthin was significantly ($p < 0.05$) and positively correlated with temperature, salinity and total P (TP), although the correlation coefficients were relatively low ($0.18 < r < 0.52$). The ratio was significantly ($p < 0.05$) and negatively correlated with dissolved inorganic N and P (DIN and DIP), dissolved organic N (DON) and total N (TN), although the correlation coefficients were also relatively low (–0.32 < r < –0.54). The pigment ratio was most highly correlated with the Ln-transformed ^{224}Ra/^{223}Ra activity ratio (r = –0.84) and water 'age' (r = 0.82, Fig. 5). As the source of these short-lived isotopes must be groundwater, this strongly suggests that SGD has a significant link to phytoplankton community structure in Little Lagoon. This is consistent with the observation that blooms of the HAB diatom *Pseudo-nitzschia* spp. at Little Lagoon Pass are correlated with groundwater elevation (Liefer *et al.*, 2009).

CONCLUSIONS

This study demonstrated the utility of Rn and Ra isotopes in identifying areas where groundwater inputs are qualitatively important as well as quantifying the SGD rates in Little Lagoon, Alabama. An overall water residence time (~10 days) was estimated using a tidal flushing model and SGD rates calculated using a mass balance of excess ^{226}Ra ranged from 0.61 to 1.56 m^3 s^{-1}. Since there are no significant surface water inputs to the lagoon and groundwater has extremely high TN and TN:TP molar ratios, SGD must dominate the N supply. Finally, the associations between ^{224}Ra/^{223}Ra ratios and microalgal community structure demonstrated the possibility that SGD acts as a driver of community composition.

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